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CONCENTRATES FROM ULTRAFILTRATION OF
BLEACHED-KRAFT EFFLUENTS**

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THE FEASIBILITY OF BURNING THE CHLORINE-CONTAINING CONCENTRATES FROM ULTRAFILTRATION OF BLEACHED-KRAFT EFFLUENTS

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ABSTRACT

Closed-cycle concentrates were simulated by laboratory-scale ultrafiltration of C/D and E1 effluents from two bleached-kraft mills. The concentrates were found to be very similar to typical kraft black liquor in carbon contents, heating values, and densities. Viscosities of concentrates were similar to or slightly above the range of typical black liquor viscosities. The C/D concentrates contained approximately 20% chlorine (weight % of moisture-free solids), while the E1 concentrates contained approximately 10% chlorine.

Upon combustion of E1 concentrates in air, all of the organic-bound chlorine was converted to inorganic chlorine and retained in the non-combustible ash. The rate of this chlorine trapping increased with increasing temperature but was zero order with respect to concentration of organic chlorine.

Burning rates for the concentrates were found to be similar to rates for black liquor burning. Volatiles yields were 46-50% (of moisture-free solids). Char yields were strongly dependent on temperature, increasing from near zero at 600 °C to 45% at 1000 °C. Overall burning rates are predicted from a global model which includes a first order rate expression for volatiles evolution and a pseudo-first order rate expression for char burning.

INTRODUCTION

There is increasing interest in moving toward closed-cycle technologies such as ultrafiltration at existing bleached-kraft mills. A number of laboratory-scale and pilot-scale studies¹⁻⁴ and at least one full-scale application⁵ have demonstrated ultrafiltration for removing color, organic carbon, and chlorinated organic compounds from bleached-kraft effluents. While these studies have shown ultrafiltration to be a potentially viable treatment technology, what has not been demonstrated is a generally accepted means of disposal of the ultrafiltration concentrate. In a recent technical bulletin,⁶ the National Council of the Paper Industry for Air and Stream Improvement identified this as one of the major technical problems associated with the ultrafiltration process.

For many mills, the logical choice for concentrate disposal would be the recovery furnace. This is reportedly the practice in the full-scale ultrafiltration application.⁵ However, data are not available concerning the effects of this chlorine-containing concentrate on important operating variables such as black liquor combustion rates, black liquor heating values, furnace emissions of HCl and chlorinated organic compounds, and corrosion of recovery cycle equipment. An alternative to disposal in the recovery furnace would be a separate thermal destruction device dedicated to concentrate disposal, such as a fluidized bed combustor or rotary kiln.

Evaluation of the feasibility of burning chlorine-containing concentrates from ultrafiltration in either a recovery furnace or in an alternative device requires information concerning the chemical compositions, physical (i.e., thermal

and transport) properties, and combustion behavior of the streams. With the exception of limited information on the chemical compositions of ultrafiltration concentrates,^{1,3,4} such data are not available. The objective of the present study has been to provide some of this needed data and to use this information to evaluate the feasibility of burning ultrafiltration concentrates. The data were obtained by laboratory-scale simulation of concentrated streams and measurements of (1) the chemical compositions and key physical properties, (2) the important combustion properties, and (3) the fate of the chlorine upon combustion of the simulated streams.

ULTRAFILTRATION PROCEDURE

Concentrates were simulated by laboratory-scale ultrafiltration of acid-stage (C/D) and caustic-stage (E1) effluents from two bleached-kraft mills. The ultrafiltration was accomplished using the plate-and-frame filtration equipment shown in Figure 1. The filtration module contained a vertical stack of membrane support plates and spacers between which the membranes were placed. Total membrane surface area was 0.72 m² (7.8 ft²).

The filtration was performed batchwise. Approximately 80 liters of C/D or E1 bleached-kraft effluent were placed in the feed tank and pumped through the filtration module. The permeate was collected while the concentrate was recycled to the feed tank, until the volume of liquid in the feed tank had decreased to approximately 2 liters (concentration factor of 40). Operating temperature and pressure were 60 °C (140 °F) and 1.0 MPa (10 atm). The membranes were polysulfone on polypropylene backing with a molecular weight cutoff of 6,000. These membranes and the operating conditions were

purposely chosen to simulate a recent pilot-scale ultrafiltration demonstration conducted at a bleached-kraft mill.² Additional details of the laboratory-scale ultrafiltration are reported elsewhere.^{7,8}

1. CHEMICAL AND PHYSICAL PROPERTIES

Compositions

Shown in Table I are the elemental compositions and heating values for the concentrates. Included in Table I for comparison are compositions and heating values for a limited number of other commonly burned materials.

I. Compositions of ultrafiltration concentrates and other fuels (weight %, moisture-free basis)

	C/D CONC.		E1 CONC.		OTHER FUELS		
	Mill A	Mill B	Mill A	Mill B	BLS ^a	MSW ^b	Coal ^c
C (total)	33.5	32.2	47.9	42.4	39.0	34.2	77.7
C (carbonate)	0.03	0.00	0.18	0.24			
H	2.54	2.38	3.58	3.37	3.8	4.5	5.0
O	31.2	31.7	30.1	34.8	33.0	27.1	6.2
S	1.84	2.91	0.59	0.58	3.6	0.3	1.6
N	0.02	0.10	0.09	0.12		0.7	1.5
Cl (total)	20.1	19.4	9.17	7.76	0.6	0.7	
Cl (organic)	7.95	4.76	5.01	4.31			
Na	5.49	4.49	8.73	11.4	18.6		
K	0.26	0.50	0.27	0.41	1.2		
Other Inorganic	3.00	3.16			0.2	32.5	8.0
TOTAL	97.93	96.94	100.3	100.8	100.0	100.0	100.0
Na/Cl Molar Ratio	0.42	0.36	1.47	2.26			
Heating Value, KJ/Kg ^d	12,400	12,000	19,200	15,300	15,400	10,400	32,300

(a) typical kraft black liquor, concentrator outlet⁹ (b) typical municipal solid wastes¹⁰
(c) typical bituminous coal¹¹ (d) HHV as determined by bomb calorimetry

Heating values reported in Table I were determined as the heat of combustion released from the exothermic conversion (higher heating value, liquid H₂O product) in an oxygen-charged bomb calorimeter. Heating values for the concentrates were similar to heating values for typical kraft black liquor, both on a moisture-free basis. This is consistent with the observation that the levels of combustible matter (i.e., carbon and hydrogen) in the concentrates were similar to the levels in black liquor. The C/D concentrate heating values were lower than the E1 concentrate heating values, again consistent with the relative levels of combustible matter in these materials. As reported by Shafizadeh and DeGroot,¹² an adequate predictor of heating value for various types of wood is carbon content. Correlation of the heating values in Table I with carbon content gives

$$\text{HHV} = 38,200 (m_c) \quad (1)$$

where HHV is the higher heating value in KJ/Kg, and m_c is the mass fraction of carbon in the material (moisture-free basis). This simple expression predicts heating values for the concentrates and for typical black liquor that are within 5.9% of the heating values measured by bomb calorimetry. Equation 1 should prove useful when an approximation of ultrafiltration concentrate heating value is needed for design purposes.

A notable difference in comparing the compositions of concentrates to those of other fuels (including black liquor) is the chlorine content. While other fuels typically contain less than 1% chlorine, the concentrates contain 8-20% chlorine. This high level of chlorine represents potential difficulties relating to fouling and plugging and relating to stack emissions of HCl and

chlorinated-organic compounds. An important consideration in this regard is the molar ratio of sodium to chlorine. As shown in Table I, the E1 concentrates have a molar excess of sodium while the C/D concentrates have a molar excess of chlorine. These proportions suggest that combustion of C/D concentrates would yield significant quantities of HCl, while combustion of E1 concentrates should yield much less HCl due to the excess Na. From this viewpoint, combustion of C/D concentrates may be less desirable than combustion of E1 concentrates. Additional discussion about this is contained in the section on the fate of chlorine during combustion.

The concentrates were found to contain less sodium and less sulfur than kraft black liquor. This may be due to the nature of the filtration treatment. Ultrafiltration tends to have higher removal efficiencies for larger molecules (such as high-molecular-weight organic compounds) and lower removal efficiencies for smaller molecules (such as ionic salts), resulting in concentrates enriched with organics and depleted of inorganics compared to unfiltered kraft liquors. For the C/D concentrates, the elements in the category labeled "Other Inorganics" in Table I were primarily calcium, silicon, magnesium, and iron.

Densities

Density was measured by weighing known volumes of concentrates at various levels of solids and temperature. The density values were found to be very similar for all of the concentrates. Density was dependent primarily on solids level and temperature. Significant differences in density were not seen among differences in mill (Mill A versus Mill B) or bleach stage (C/D

versus E1). This is similar to the conclusion of Fricke¹³ that densities for kraft black liquors do not vary significantly from one black liquor to another.

Measured density values are shown in Figure 2 for one of the concentrates. Density decreased with increasing temperature, showing approximately a linear dependency. The increase in density with solids was also approximately linear. These observations suggest that a single linear correlation will describe the density data in terms of these two factors. A least-squares regression based on the density data for both E1 and C/D concentrates gives the following expression relating density to temperature and solids,

$$\rho = 1008 + 6.3 (S) - 0.42 (T), \text{ kg/m}^3 \quad (2)$$

where S is weight percent solids, and T is degrees C. Equation 2 predicts values for density of the concentrates which are, in all cases, within 3.1% of the measured values.

This expression (Equation 2) is nearly identical to previously reported correlations for black liquors. Fricke¹³ has reported the density of seven kraft black liquors at 25 °C as $997 + 6.49 (S)$; and Venkatesh and Nguyen¹⁴ report that the density of black liquor is $1007 + 6.0 (S) - 0.495 (T)$. The similarity of these expressions to Equation 2 suggests that the densities of concentrates from bleached-kraft effluents are essentially identical to the densities of kraft black liquors.

Viscosities

Viscosities were measured as kinematic viscosity by observing the time required for gravity drop (free fall) of the fluid through a calibrated bulb. Kinematic viscosity values were multiplied by density values (calculated from Equation 2) to give viscosity. Results for E1 concentrates are shown in Figure 3 at five temperature levels between 25 and 100 °C and at various solids levels (up to 40%). Viscosities were not measured for C/D concentrates, since attempts to increase the solids level beyond about 4 weight% resulted in formation of precipitates which prevented accurate viscosity determination. No testing was performed to evaluate viscosity as a function of shear rate. It has been shown for black liquor that, for solids levels up to 50%, viscosity does not depend on shear rate in the range of shear rates typical of mill operating conditions.^{9,13} Based on this, it was presumed that there was little need to investigate shear rate dependency for the viscosity of ultrafiltration concentrates.

In general, viscosity was found to increase with increasing solids and to decrease with increasing temperature. Solids and temperature were not the only factors affecting viscosity, as values were found to vary by more than an order of magnitude among concentrates at similar conditions of solids and temperature. For example, Figure 3 shows that, at 25 °C, viscosity is over 1000 cP for E1 concentrate from Mill A at 29.3 % solids, while it is less than 50 cP for E1 concentrate from Mill B at 36.2 % solids. With the information available, it was not possible to establish what the other factors are, though it is expected that wood species, pulping conditions, and bleaching conditions each play some role. The variation in viscosity among similar concentrates

was much less noticeable at solids levels below 10%. This is probably because the organic phase plays a diminishing role in the resulting fluid rheology as solids level decrease.

Included in Figure 3 is viscosity predicted for black liquor based on the equation of Adams and Frederick,⁹ which is,

$$\log (\mu_{bl}) = \log (\mu_w) + 1.51 \times 10^{-2} (S)(T^*/T) + 2.61 \times 10^{-7} [(S)(T^*/T)]^{3.72} \quad (3)$$

where μ_{bl} is the black liquor viscosity (Pa-s), S is the liquor solids (percent), T is the liquor temperature (K), T^* is a reference temperature (373 K), and μ_w is the viscosity of pure water at the liquor temperature. Adams and Frederick state that black liquor viscosity is affected by wood species and type and by pulping conditions; and that viscosity predicted by Equation 3 can vary by a factor of five from the true viscosity. As shown in Figure 3, this equation underpredicts viscosity by a factor of about 3.5 for Mill B E1 concentrate and by a factor of 10-100 for Mill A. Based on this comparison, it appears that viscosities of ultrafiltration concentrates from bleached-kraft effluents are similar to or higher than viscosities of kraft black liquors. This could be related to molecular weight, since the ultrafiltration concentrates should contain a greater fraction of higher molecular weight compounds than unfiltered kraft liquors.

Other Physical Properties

Other thermal and transport properties which are integral to the evaluation, design, and optimization of the unit operations involved in thermal

destruction of chlorine-containing concentrates are heat capacity, thermal conductivity, solubility, boiling point rise, and surface tension. Values of these properties were not investigated and have not been reported elsewhere in the literature. Given the similarities already shown between these concentrates and kraft black liquors, a reasonable alternative for estimating values of these properties would be to use the methods and relationships discussed by Adams and Frederick⁹ for estimating black liquor thermal and transport properties.

2. COMBUSTION PROPERTIES

With regard to burning chlorine-containing concentrates, the combustion characteristics of greatest interest are: (1) the relative yields or amounts of volatile combustible matter (volatiles), non-volatile combustible matter (char), and non-combustible matter (ash); (2) the combustion rates; and, (3) the characteristics of the non-combustible ash, such as ash melting temperature and ash chemical composition. Data were obtained illustrating these combustion characteristics for one of the concentrates (Mill B E1 concentrate).

Relative Yields

The yields of volatiles were determined by heating samples of moisture-free solids in alumina crucibles. The crucibles were sealed with lids during heating to prevent air from entering and oxidizing the solids. Heating rates were moderate, approximately 15 K/s. Heating time was 15 minutes. Volatiles yields were identical at 600 °C for heating times of 15 minutes and 30

minutes, demonstrating clearly that 15 minutes was sufficient time to drive off all the volatiles. Total yields were determined in a similar manner except that the heating times were 60 minutes, and the crucible lids were not used so as to expose the crucible contents to air for oxidation. Char yields were determined by subtracting volatiles yield from total yield. The yields so obtained are shown in Figure 4.

Volatiles were found to account for about one-half (46-50%) of the moisture-free mass. Volatiles yield was not strongly dependent on final heating temperature, though some increase is apparent up to 900 °C. This trend confirms the thermogravimetric data reported earlier,⁷ which show that, for similar concentrates, nearly all of the mass loss in the absence of air occurred at temperatures between 200 and 550 °C, with very little additional volatiles mass loss occurring at temperatures greater than 600 °C. These volatiles yields may be somewhat lower than would be obtained in practical furnaces. It has been shown in coal pyrolysis experiments¹⁵ that coal volatiles yield is greater for rapid heating rates (10^5 - 10^6 K/s). With this in mind, the volatiles yields of Figure 4 should probably be considered as minimum values.

At lower temperatures, the combustion mass loss was dominated by volatiles evolution, while at higher temperatures, combustion mass loss was about one-half volatiles evolution and one-half char burning. Char yields increased dramatically in the temperature range 600-700 °C and appeared to approach asymptotically a limiting value of approximately 45% as temperature increased beyond 700 °C. Thus, combustion mass loss increased with temperature to the point where nearly all (approximately 95%) of the initial mass was vaporized at 1000 °C.

Combustion Rate Data

Isothermal mass loss experiments yielded burning rates in air at three temperatures, 600, 700, and 800 °C. These data were obtained using the specially designed flow-through crucible shown in Figure 5. The crucible was made of fused quartz to minimize interfering reactions at the high temperatures and strongly oxidizing conditions. For each determination the crucible was charged with a known mass of finely ground solids (approximately 50 mg). The crucible with sample was placed in a preheated muffle furnace on ceramic blocks. The floor of the crucible was a fritted piece which retained the particles and allowed air to flow by natural convection through the sample during heat-up. Particle heating occurred due to convection/conduction from the gas and heat release from exothermic reactions. After the desired combustion time had elapsed, the crucible and contents were removed from the furnace and cooled. The residue remaining in the crucible after this heat treatment was weighed and compared with the initial weight to determine mass loss.

The resulting isothermal mass loss data are shown in Figure 6, where the ordinate is the fraction of initial moisture-free mass remaining after heating in air. Each of the three isothermal curves shows a very rapid rate of mass loss in the first 50-100 seconds of combustion time corresponding to volatiles evolution. This was followed by a less rapid rate of mass loss at longer combustion times corresponding to heterogeneous char burning. The total yield increased significantly with increasing temperature. Total yields at combustion times greater than 500 seconds correspond reasonably well at these three temperatures with the yield data shown in Figure 4. The total

yield for the 600 °C isotherm indicates that little char burning occurred at this temperature, since the mass loss never exceeded the maximum fraction of volatiles.

The effect of particle heat-up time can be seen in each of the three isotherms. This is the reason for the slower rate of mass loss at times less than 20 seconds. A value for effective heat-up time was estimated by extrapolating the steepest portion of each isotherm (which is in the range of 15-50 seconds) to a mass fraction of unity. This showed that, for all three temperatures, the effective heat-up time was approximately 15 seconds. This is consistent with heat transfer calculations which indicated that particle heat-up time was in the range of 5-20 seconds.

Combustion Rate Model

By assuming that mass loss due to char burning was negligible over the relatively short time period of volatiles evolution, the slope in the range of 15-50 seconds for each mass-loss curve was used to estimate a first order Arrhenius law rate constant for volatiles evolution

$$k_v = -(dm_v/dt)/m_v \quad (5)$$

where m_v is the mass fraction of volatiles and $-dm_v/dt$ is the rate of volatiles evolution with respect to time, t . This form of rate model was selected based on previous coal combustion studies which showed that coal pyrolysis can be represented approximately by a single Arrhenius law equation, which is useful for design purposes.¹⁶ Similarly, a pseudo-first order rate constant for

char burning in air is estimated from the slopes of the 700 and 800 °C isotherms at times greater than 100 seconds as,

$$k_C' = k_C y_{O_2} = -(dm_C/dt)/m_C \quad (6)$$

where m_C is the mass fraction of char, $-dm_C/dt$ is the rate of char burning with respect to time, and y_{O_2} is the mole fraction of oxygen in the combustion air. Again, this form of model was selected based on previous coal combustion studies which showed that coal char combustion can be adequately represented by a single Arrhenius law rate expression.¹⁵ Values determined in this manner for k_V and k_C' are plotted in Arrhenius law form in Figure 7. Fitting of these rate constants to an Arrhenius expression with temperature activation gives

$$k_V = 3.6 \exp [-8,300 \text{ cal/gmol} / (RT)], \text{ s}^{-1} \quad (7)$$

and

$$k_C' = 22 \exp [-18,000 \text{ cal/gmol} / (RT)], \text{ s}^{-1} \quad (8)$$

These rate expressions (equations 5 and 6) can be combined to give a simplistic overall model for burning rate. At any time during burning of an initial mass (m_i) of moisture-free solids, the unburned mass (m) could be thought of as consisting of three parts: volatilizable mass (m_V), non-volatile combustible mass (m_C), and non-combustible mass (m_A); that is,

$$m = (m_V + m_C + m_A) \quad (10)$$

By definition, the non-combustible content is constant at a given temperature and can be alternatively expressed as

$$m_a = (m_i - m_{V\infty} - m_{C\infty}) \quad (11)$$

where $m_{V\infty}$ is the maximum potential mass of volatiles and $m_{C\infty}$ is the maximum potential mass of char. Substitution of this expression (Equation 11) into Equation 10 and dividing through by m_i gives the following model for overall burning rate:

$$X = 1 - X_{V\infty} [1 - \exp(-k_V t)] - X_{C\infty} [1 - \exp(-k_C y_{O_2} t)] \quad (12)$$

where X is the fraction of mass remaining unburned, $X_{V\infty}$ is the maximum potential mass fraction of volatiles, and $X_{C\infty}$ is the maximum potential mass fraction of char. This model states simply that the mass remaining unburned is the initial mass minus the losses due to volatiles evolution and heterogeneous char burning. Values for the $X_{V\infty}$ and $X_{C\infty}$ are readily obtained from Figure 4 or from the following expressions which were determined from regression of the data in Figure 4:

$$X_{V\infty} = 0.42 + 6.6 \times 10^{-5} (T) \quad (13)$$

and

$$X_{C\infty} = 0.43 - 2710 \exp [-1.02 \times 10^{-2} (T)] \quad (14)$$

where T is the final heating temperature in Kelvin. Values of k_v and k_c' are obtained from Equations 7 and 8.

Predictions using Equation 12 were made for E1 concentrate from Mill B and are shown in Figure 6 as solid lines. As seen in Figure 6, the model predicts the overall burning rates very well. This close agreement supports the assumptions made in the model development that volatiles evolution and char burning rates are approximately first order with respect to the volatiles and char masses remaining in the unburned material. In applying this model, it should be kept in mind that it is not a fundamental kinetic description of devolatilization or char burning, both of which undoubtedly involve multiple elementary reaction steps. The model should prove useful for design purposes or whenever an approximation of ultrafiltration concentrate burning rates is required.

Included in Figure 7 for comparison is the rate of kraft black liquor char burning in air as determined by Grace et al.¹⁷ The rates of concentrate char burning and black liquor char burning are quite similar over the range of typical combustion temperatures, and are identical at a temperature of 1000 °C. The activation energy is higher for the black liquor char. Since the slower step in the combustion of these materials is char burning, it is reasonable to conclude that the solids from ultrafiltration of bleached-kraft E1 effluent burn at a rate comparable to that of kraft black liquor solids.

Ash Compositions

As defined earlier, ash is the non-combustible portion of the concentrate solids. This definition is somewhat arbitrary because it depends on the combustion temperature, a higher temperature giving lower ash values. As shown in Figure 4, ash yields decreased from nearly 50% of the initial mass at 600 °C to less than 10% at 1000 °C. It is important to know the composition of the ash and the melting temperature as these factors will have tremendous impact on the chloride buildup and corrosion in a recovery furnace and on the behavior of the non-combustible ash in any alternative combustion technology.

Detailed composition is shown in Table II for ash remaining after burning a sample in air at 700 °C for one hour.

II. Ash composition, Mill B E1 concentrate

<u>component</u>	<u>weight %</u>
Na	32.7
Cl	26.6
CO ₃ ⁼	11.7
SO ₄ ⁼	4.67
Si	3.32
K	1.71
Ca	1.40
Al	0.61
Mg	0.16
Fe	0.03
Cu	<u>0.02</u>
	82.9

The majority of the ash was found to be sodium and chloride. There were also significant levels of carbonate and sulfate and lesser amounts of other metals. The remainder of the ash (not accounted for in Table II) was probably oxygen in the form of metal oxides. Estimates of the ash melting temperatures showed initial deformation at approximately 700 °C and complete melting at approximately 800 °C. The melting point of pure NaCl is 801 °C.

These melting point data suggest that fluidized bed combustion may be an attractive technology for concentrate treatment, since it could be operated at low enough temperatures to prevent melting of the inorganics. Removal of solids from the fluidized bed would then serve as the means of effective removal of chlorine from the system. The long solid-phase residence times and complete mixing which are characteristics of fluidized beds would ensure a high level of destruction of organic compounds.

The presence of sulfate in the ash may provide additional insight regarding the char burning rates presented previously. Grace et al.¹⁷ showed clearly that kraft char burns about an order of magnitude faster than soda char due to the presence of sulfate in the kraft char, which oxidizes char carbon. It seems reasonable that the presence of sulfate during burning of ultrafiltration concentrates helps to explain why the burning rates were found to be comparable to burning rates for kraft black liquor solids.

3. FATE OF CHLORINE

In burning materials which contain significant levels of chlorine, there is potential for emissions of HCl and chlorinated organic compounds. Trace levels of such compounds, including polychlorinated dibenzodioxins and dibenzofurans, have been measured in the gas and solid emissions of a wide variety of chlorine-containing waste incineration facilities.¹⁰ This has resulted in a high level of public awareness and concern related to combustion of chlorine-containing fuels. For this reason, it is important to quantify the fate of chlorine upon combustion of chlorine-containing concentrates from bleached-kraft effluents.

Isothermal mass loss measurements at 600 and 700 °C were used to determine the fate of the chlorine in burning the E1 concentrates. The same procedure was used for heat treatment of small (50 mg) samples as described in the previous section for combustion rate measurements. The residue remaining after heating was dissolved in a known volume of water and the AOX concentration determined for this solution was used as a direct measure of the amount of organic chlorine in the residue. Similarly, the chloride concentration was determined for the solution by ion chromatography and used as a direct measure for the amount of inorganic chlorine in the residue. The sum of organic chlorine and inorganic chlorine was considered as the total chlorine. The results are shown in Figure 8.

Chlorine Trapping

As seen by the solid bars in Figure 8, the amount of organically bound chlorine decreased sharply as the samples were heated. The combustion time required for essentially complete disappearance of the organic chlorine was 50 seconds at 600 °C and 35 seconds at 700 °C. At both temperatures, the disappearance of organic chlorine was mirrored by an increased level of inorganic chlorine such that the total chlorine mass in the unburned residue remained nearly constant. Thus, the fate of the organic chlorine was not conversion to HCl, but rather the organic chlorine was trapped in the non-combustible ash as inorganic salts, primarily NaCl. This observation of "chlorine trapping" is significant because it implies that burning of chlorine-containing concentrates will pose less potential for emissions of HCl and chlorinated organic compounds when the concentrate contains a molar excess of sodium over chlorine.

Chlorine trapping has also been observed by Sasaki et al.¹⁸ during pyrolysis of chlorinated thiolignin when alkali was present. Upon pyrolysis at 710 °C in N₂ gas with no alkali present, 90% of the total chlorine was recovered in the vapor products as HCl, 5-10% as methyl chloride, and only 2-5% remained in the char residue as NaCl. With alkali addition (as NaOH) the fate of the chlorine during pyrolysis was remarkably changed. With enough alkali added to the chlorinated thiolignin such that the Na/Cl molar ratio was 1.0, 99% of the total chlorine remained in the char residue as NaCl.

Rate of Chlorine Trapping

It is apparent from the data in Figure 8 that the rate at which chlorine trapping occurred was not dependent on the mass of organic chlorine remaining. At a given temperature, the rate was approximately constant until the trapping was complete. Since the experiments of Sasaki et al.¹⁸ were done in inert gas, the rate of chlorine trapping is evidently not dependent on oxidizer concentration in the gas. These observations suggest a zero-order dependent rate expression of the form

$$-(dX_{O-Cl})/dt = k_{O-Cl} \quad (15)$$

where X_{O-Cl} is the mass of organic chlorine divided by the initial mass of organic chlorine. Using the data in Figure 8, values of k_{O-Cl} are 0.020 and 0.033 reciprocal seconds at 600 and 700 °C, respectively. Assuming the rate of chlorine trapping to be temperature activated, these two rate constant values are fit to an Arrhenius' law expression to give

$$k_{O-Cl} = 2.86 \exp [-8,600 \text{ cal/gmol}/(RT)], \text{ s}^{-1} \quad (16)$$

Integration of Equation 15 yields an expression for X_{O-Cl} as a function of reaction time and temperature. Substituting the result of this integration into an expression for the extent of chlorine trapping yields

$$TE = 100\% (1 - X_{O-Cl}) = 100\% (k_{O-Cl}t) \quad (17)$$

where TE is defined to be the chlorine Trapping Efficiency, or the percentage of initial organically bound chlorine that has been converted to inorganic form. Values for TE predicted by Equation 17 are shown in Figure 9 for various temperatures. This information will be useful in predicting the fate of chlorine in a combustion process dedicated to burning concentrates. In a recovery furnace, mixture of the chlorine-containing concentrates with black liquor provides opportunity for many other species to compete with the chlorine in forming compounds with the available sodium. Thus, it is not expected that quantitative chlorine trapping would occur when burning concentrates in the recovery furnace; nevertheless, because of the high level of sodium in black liquor, some trapping will occur, and it is expected that HCl emissions will be much less than if no sodium were present.

Chemical Equilibrium

Chemical equilibrium predictions of the major chlorine-containing species from combustion of ultrafiltration concentrates are shown in Figure 10. Equilibrium predicts a similar fate for the chlorine as that observed both in this study and in the study of Sasaki et al.¹⁸ Without sodium present, chemical equilibrium predicts that nearly all of the chlorine is emitted as HCl with small amounts of Cl₂ (not shown in Figure 10). As sodium content is increased, equilibrium concentrations of HCl decrease while NaCl concentrations increase, until essentially all of the chlorine is accounted for as NaCl. These calculations were based on the moles of C, H, O, Na, Cl, and S in the fuel (concentrate), moles of O and N in the oxidizer (air), initial energy state (heats of formation for fuel and oxidizer at 298 K), and pressure as input. For these conditions and mole constraints, the composition of products

which yielded the lowest free energy state was determined. Over fifty chlorine-containing species were considered as possible products.

CONCLUSIONS

The chemical compositions and physical properties of chlorine-containing concentrates from ultrafiltration of bleached-kraft effluent were found to be similar to kraft black liquor in many respects. Heating values of E1 concentrates were similar to or higher than heating values for typical kraft black liquor, while heating values for C/D concentrates were about 20% lower. Densities of ultrafiltration concentrates were essentially identical to kraft black liquor densities and can be accurately predicted from knowledge of the liquor solids and temperature. Viscosities of ultrafiltration concentrates were similar to or slightly greater than viscosities of kraft black liquor. Viscosities differed by more than one order of magnitude for two E1 concentrates at similar solids and temperature levels, indicating effects of other factors on viscosity and making it difficult to predict viscosity accurately.

Concentrate compositions differed from kraft black liquor composition, most notably in chlorine content. Chlorine levels were approximately 10% and 20% of the moisture-free solids for E1 and C/D concentrates, respectively, while black liquor chlorine levels are typically less than 1%. Other differences were levels of sulfur and sodium. The E1 concentrates contained only about 15% as much sulfur as black liquor. Both C/D and E1 concentrates contained half or less than half as much sodium as black liquor.

Analysis of relative combustion yields for E1 concentrates showed volatiles yields to be in the range of 46-50% of the moisture-free solids mass, increasing slightly with temperature between 500 and 1000 °C. Char yields were strongly dependent on temperature, increasing from near zero at 600 °C to 45% at 1000°C. The non-combustible ash was shown to consist primarily of sodium, chloride, carbonate, and sulfate. Ash melting temperatures were approximately 700 °C for initial deformation and 800 °C for complete melting.

Burning rate isotherms for E1 concentrates showed an initial very rapid mass loss corresponding to volatiles evolution followed by a less rapid mass loss after volatiles evolution was complete, corresponding to heterogeneous char burning. Overall combustion rates are adequately described by a two-part model. This model contains an expression for volatiles evolution rate which is first order dependent on the mass of volatilizable material remaining in the unburned solid, and a second expression for char burning rate which is first order dependent on both the mass of unburned char and on the bulk oxygen concentration in the gas. The combustion rates of E1 concentrates were comparable to combustion rates of kraft black liquor.

Upon combustion of E1 concentrates, the organic-bound chlorine was converted to inorganic chlorides. This result is significant because it implies minimal emission of HCl and toxic chlorinated organic compounds (when E1 concentrate is the only fuel). This phenomenon was given the designation "chlorine-trapping." The rate of chlorine trapping was constant at a given temperature, until complete disappearance of the organic-bound chlorine. A zero order model was used to adequately approximate the rate and extent of chlorine trapping.

The similarities between concentrates and black liquor suggest that combustion of ultrafiltration concentrates with black liquor in the recovery furnace may be feasible, as long as adequate chloride purge can be maintained to prevent excessive chloride buildup and de-rating of black liquor heating value. Further experiments should be completed, burning mixtures of concentrates with black liquor to evaluate the effects on emissions of HCl and toxic chlorinated-organic compounds.

Combustion of E1 concentrates in alternative devices appears feasible, since the heating values are relatively high (compared with black liquor) and since chlorine trapping will quantitatively convert the organic-bound chlorine to NaCl. The melting point data suggest that fluidized bed combustion may be the most attractive alternative technology, since it could be carried out at low enough temperatures to prevent melting of the inorganics. The long solid phase residence times and complete mixing which are characteristics of fluidized beds would ensure both a high level of destruction of organic compounds and a high level of chlorine trapping efficiency. Further work should be completed to investigate fluidized bed combustion of chlorine-containing concentrates.

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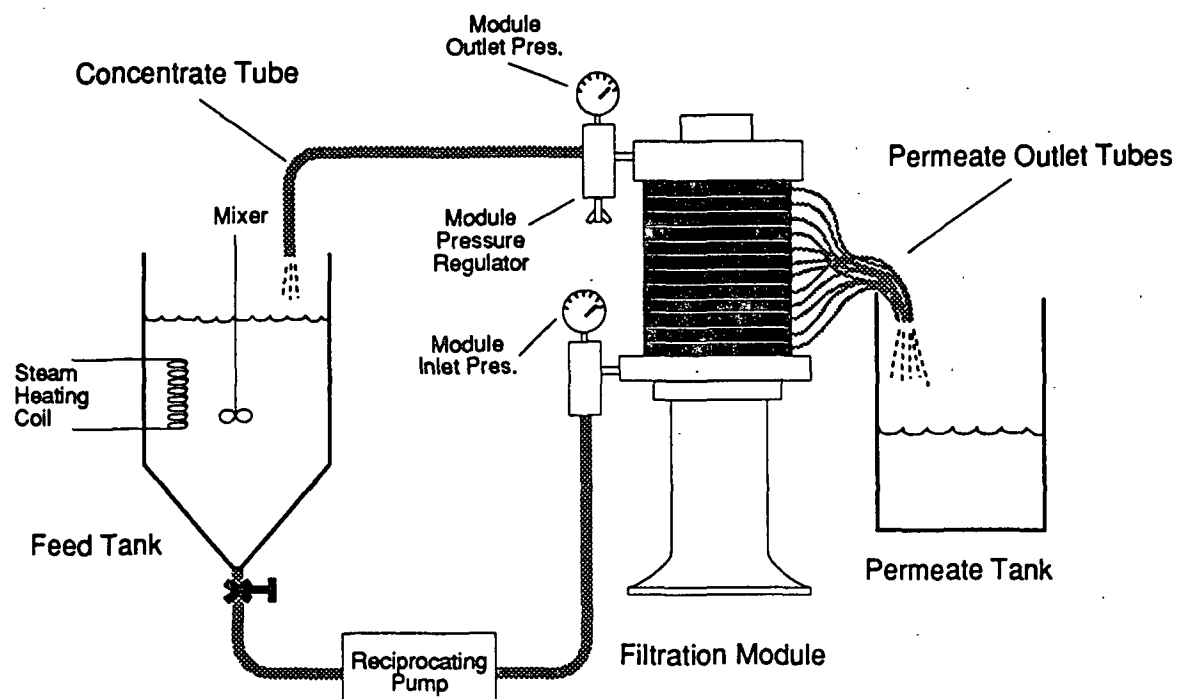


Figure 1. Laboratory-scale ultrafiltration equipment.

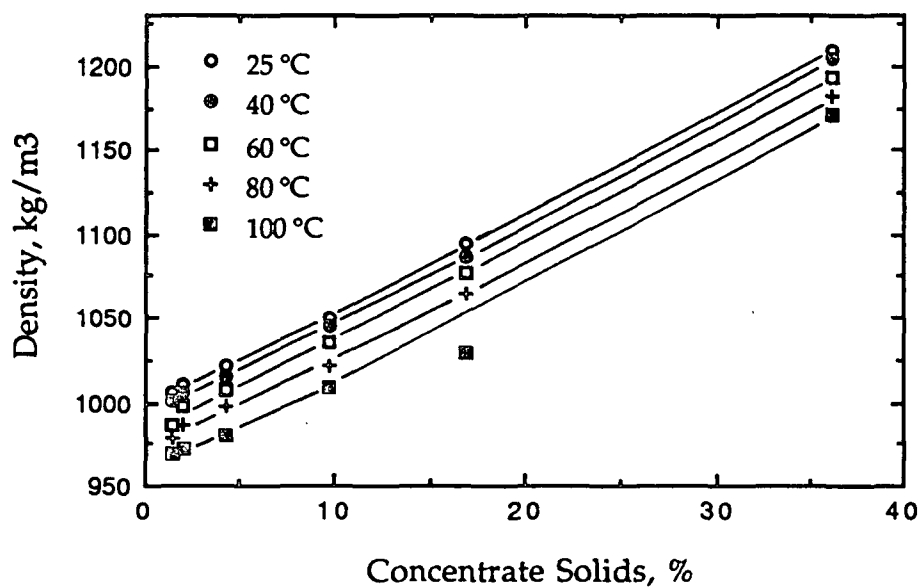


Figure 2. Densities of E1 concentrates (Mill B).

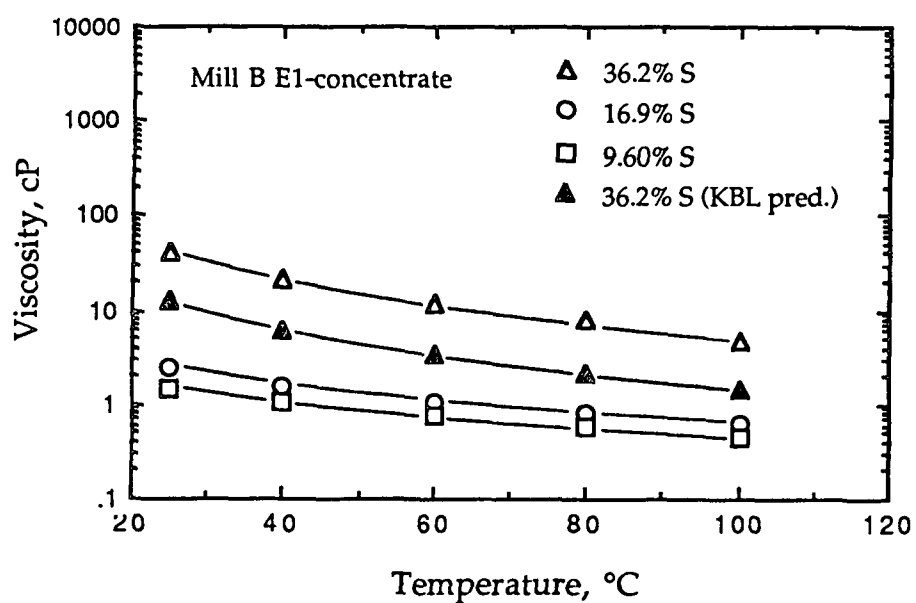
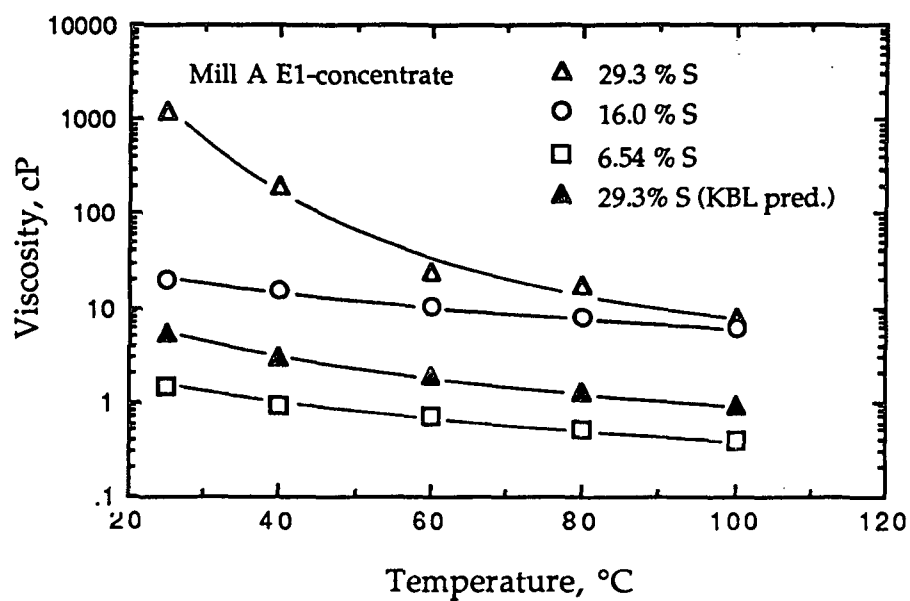


Figure 3. Viscosities of E1 concentrates (Mill A top, Mill B bottom).

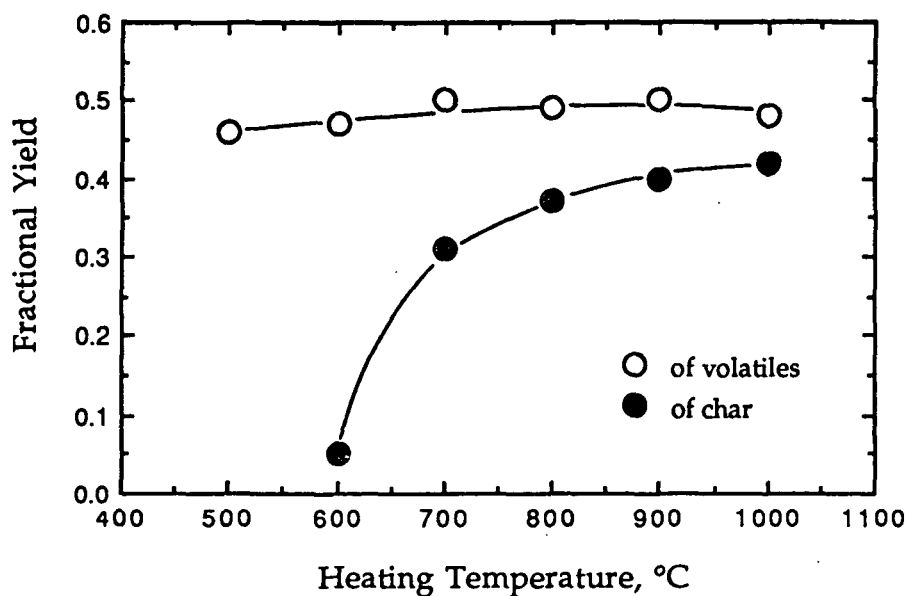


Figure 4. Relative yields of E1 concentrates, Mill B (moisture-free solids).

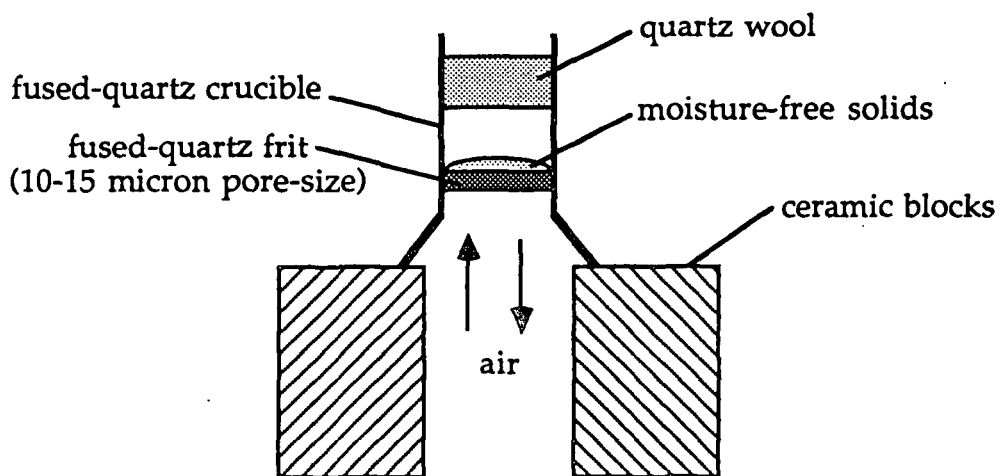


Figure 5. Flow-through crucible for isothermal weight loss measurements.

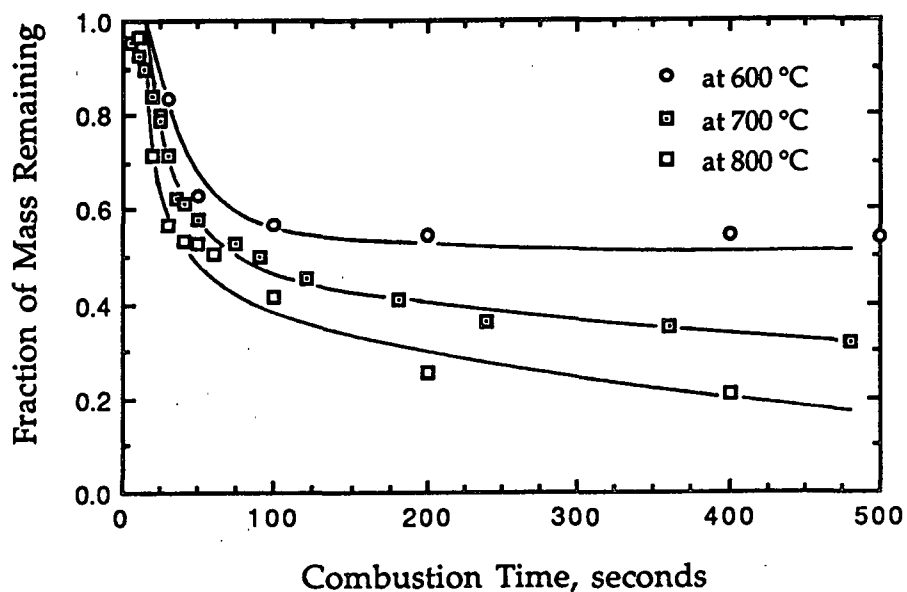


Figure 6. Weight loss during isothermal combustion in air of E1 concentrate, Mill B.

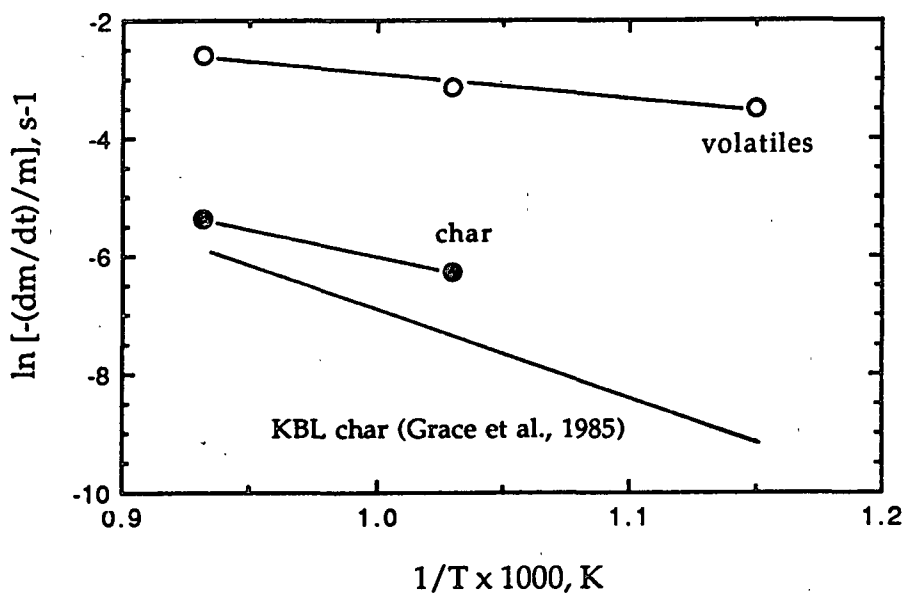


Figure 7. First order rate constants for volatiles evolution and char burning.

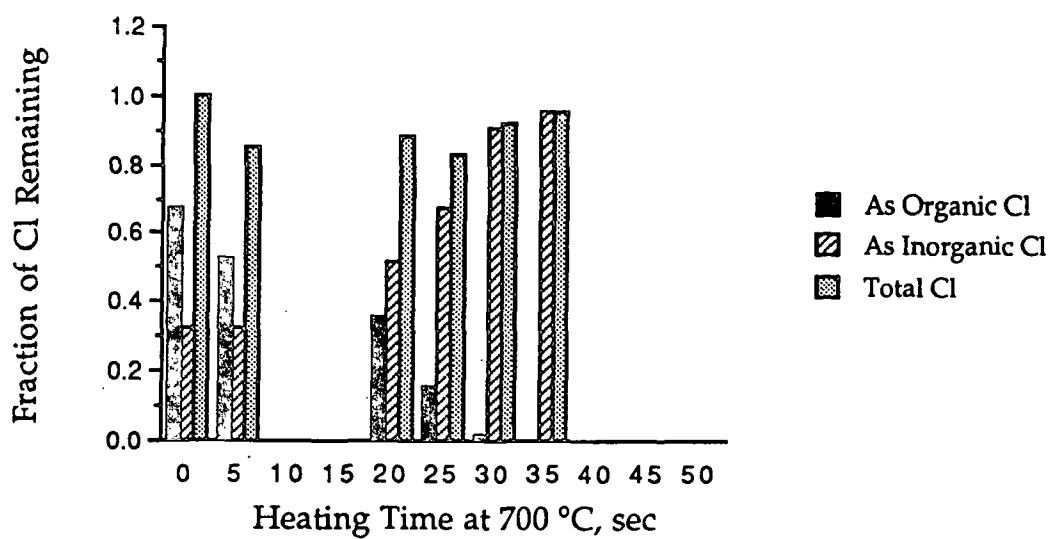
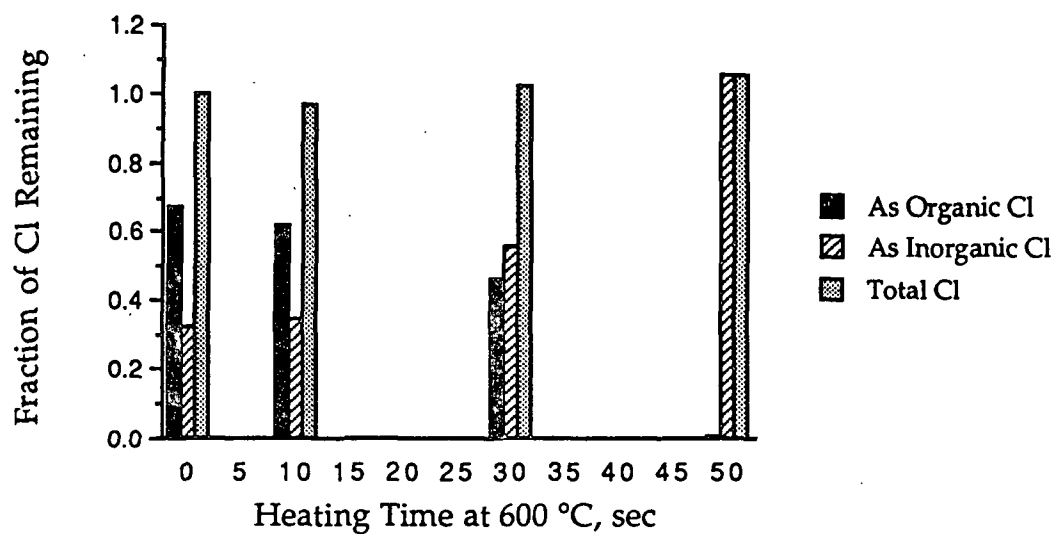


Figure 8 . Trapping of organic-chlorine during combustion in air of E1 concentrate, Mill B.

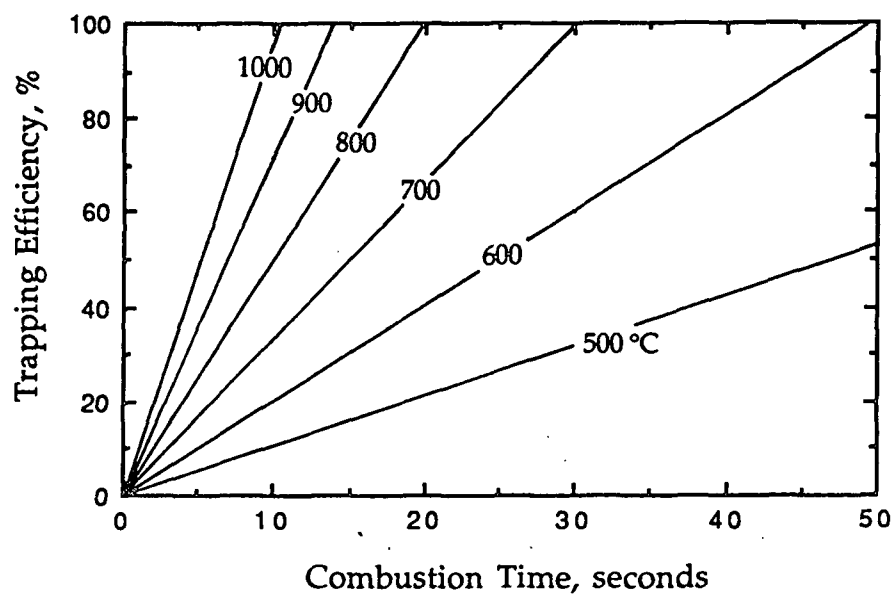


Figure 9. Predicted chlorine Trapping Efficiency.

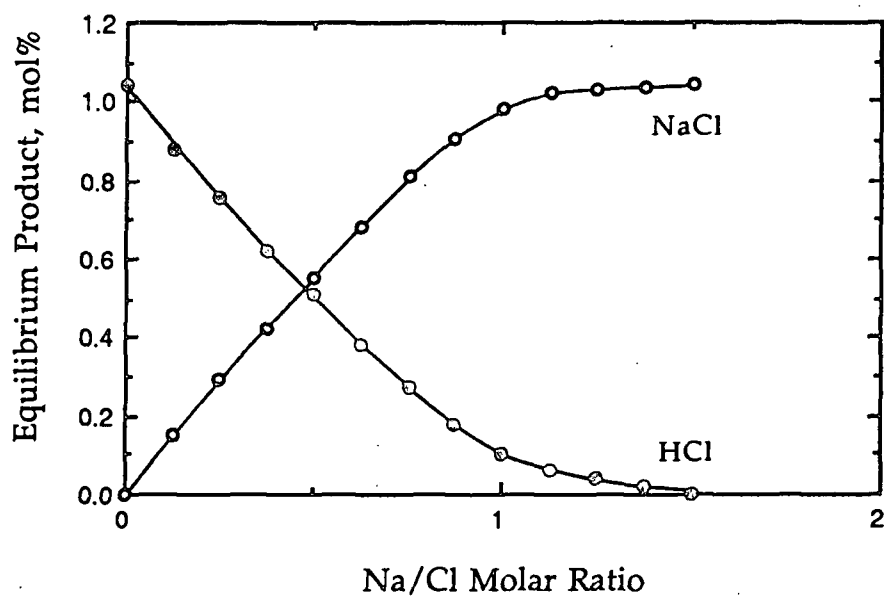


Figure 10. Chemical equilibrium prediction of fate of chlorine.